

“A Study of the Radio-activity of certain Minerals and Mineral Waters.” By Hon. R. J. STRUTT, Fellow of Trinity College, Cambridge. Communicated by LORD RAYLEIGH, O.M., F.R.S. Received February 29,—Read March 10, 1904.

PART I.

A considerable number of minerals are known in varying degrees to be radio-active. Lists have been given by M. and Madame Curie,* and by Sir W. Crookes.† Except in the case of pitchblende, little has been done to determine the nature of the radio-active constituents; or to decide whether any hitherto unknown radio-active body is present.

To obtain complete information on these subjects, the only method available would be to completely analyse the mineral, and examine every precipitate and filtrate for radio-activity. This process is of course very tedious, and the results have to be interpreted with care, since traces of radio-active elements may often be carried down in the groups to which they do not properly belong, and thus cause confusion. A much easier method is to heat the crude mineral, and to examine the rate of decay of the emanation which it gives off. Each emanation has a characteristic time-constant of decay, and by determining this we can identify it.

The method is of course useless for testing the presence or absence of radio-active elements such as uranium,‡ which do not give off a characteristic emanation. But the great facility with which it may be applied to a small quantity of material, and the definiteness of the results, are great merits.

In any case, when a material suspected to contain radium is obtainable in abundance, it is better to test for the presence of emanation than to look for activity in the solid. For but little of the solid material can be advantageously used in the test. Thick layers give no larger effect than thin ones, since the upper layers absorb the radiation from the lower. But the emanation can be extracted from any desired bulk of material, and the effect proportionately increased. If carbonic acid, or any other gas, is evolved at the same time in inconvenient quantities, it can be absorbed with a suitable reagent, and the emanation contained in it thereby concentrated.

* ‘Thèse présentée à la Faculté des Sciences,’ Paris, p. 19.

† ‘Roy. Soc. Proc.,’ vol. 66, p. 411.

‡ I have found a distinct, though feeble, emanation from re-crystallised uranium nitrate, having a rate of decay equal to that of the radium emanation. Whether this is really due to uranium, or to traces of radium, which the uranium still contains, must be left for the present an open question.

The present paper gives the results of an examination of certain radio-active materials by this method.

No new emanation has been recognised. The results have in all cases been attributable to thorium and radium.

If any emanation decidedly more permanent than that of radium existed in the evolved gas, the method could not fail to detect it. For in every case the activity of the gas was watched until it became comparable with the very small activity due to the walls of the vessel. If a more durable emanation had been present even in small quantities, the proportion of it present would have increased relatively to the radium emanation, and its presence would have become apparent towards the end, by a diminished rate of decay.

Small quantities of an emanation less durable than that of radium might have escaped detection. For they would have been masked by the much greater quantity of the latter.

By measuring the rate of leak due to the accumulated emanation from a weighed amount, the proportion of radium present may be estimated. A comparison with the leak due to the emanation of a known weight of radium must of course be made. For this purpose it would be best to weigh out, say, a milligramme of radium bromide, dissolve it in a litre of water, and evaporate a small measured quantity of the solution in a suitable tube. In this way the effect due to a standard quantity could be determined.

The method of experimenting was as follows:—

The powdered mineral was placed in a hard-glass combustion tube, drawn out and sealed at one end, connected to a mercury gas-holder at the other. The mineral was heated to redness, and the gaseous products collected in the gas-holder. When the evolution of gas had ceased, the point was broken off, and air drawn into the gas-holder, up to a standard volume.

For measuring the electrical effects, an electroscope was used. This was exhausted, and the gas extracted from the mineral, together with the air, which had been used to make up its volume to a sufficient amount, was admitted. After a few hours, enough for the deposited activity to attain its full value, the rate of leak was read. The day and hour was noted, and the gas was pumped out into a test-tube and stored over mercury. After a sufficient time had elapsed, it was again introduced into the apparatus by means of a syphon gas pipette* and the rate of leak again measured. In the meantime the apparatus had been available for making measurements with other gases.

In some cases the emanation was initially so strong that it could not be conveniently investigated. In such cases a portion of the gas was diluted with air for measuring the rate of decay at first. The

* The methods of manipulation used in storing and transferring the gases without loss were those described in Dr. Travers' book, 'The Study of Gases.'

concentrated material was kept until, by lapse of time, it had become weak enough to be conveniently used. Its activity was followed until it had become too small for measurement.

With this preface the results for the various minerals tried may be given in the form of a table. The rates of leak are given in scale divisions per hour. When air alone filled the apparatus, the rate of leak was 2·25 sc. div. per hour. This was in each case subtracted.

Mineral.	Locality.	Quantity taken in grammes.	Rate of leak due to emanation (sc. div. per hour).	Rate of leak per 100 grammes.	Time in days taken by the emanation to fall to half its initial value.
Samarskite .	N. Carolina, U.S.A.	20	20,600	103,000	3·48
Fergusonite.	Norway ?	7	4,280	61,000	3·80
Pitchblende.	Cornwall.....	40	11,900	29,800	3·50
Malacone ..	Hitteroe, Norway ..	20	1,440	7,200	3·81
Monazite...	Norway	51	2,060	4,000	3·50
„ ...	N. Carolina	82	37	45	3·81
„ ...	Brazil	54	11	24	3·80
Zircon.....	N. Carolina	60	24·6	41	4·05

All the minerals give radium emanation, though in very varying quantity.

These tests were not started quickly enough to give information as to the presence of a very quickly decaying emanation. This was tested for independently.

The mineral malacone is of peculiar interest, because it has been found to contain argon as well as helium.* Helium is formed by the degeneration of radium, and it is reasonable to assume that the other kindred gases have had a similar origin. It was hoped, therefore, that malacone might contain some new radio-active element. It is still possible that it does so, but, if so, this substance gives no emanation distinct from that of radium.

The meteorite of Augusta Co., Virginia, has also been found to contain argon and helium. But no emanation at all could be obtained from 20 grammes of it.

The minerals were all tested for thorium emanation by drawing air over them in the cold; the only one in the above list that gives it is the Norwegian monazite, and even this does not yield it very abundantly. A crystal of thorite, however, kindly lent me by Professor Lewis, was found to give torrents of thorium emanation.

* Ramsay and Travers, 'Roy. Soc. Proc.,' vol. 64, p. 131.

Air drawn over it in the cold possesses strong discharging power. It was not permissible to heat the specimen, which might have injured it, so that the presence or absence of radium emanation in thorite could not be investigated.

There can be no doubt that the other specimens of monazite contained thorium, for they were given me by the late Mr. W. Shapleigh, who was connected with the thorium industry, and used these varieties of monazite for preparing thoria. They were, moreover, markedly radio-active, while the amount of radium emanation obtained from them was so small that their activity could not be mainly due to radium. They probably contain the thorium in what Rutherford and Soddy call the de-emanated condition. That is, the thorium emanation, though formed, is not able to escape.

It is a remarkable fact that these varieties of monazite, though they contain practically no radium, yield helium in fair quantity. There are several explanations possible. The radium originally present may have almost completely decayed into helium, and any other products which it may yield; or it may be that thorium, as well as radium, yields helium by its decomposition; or, lastly, the helium may not, in this instance, have been generated by radio-active changes at all.

It is interesting to know whether the minerals retain all the radium emanation which they generate when heat is not used to expel it. Two cases were examined. One hundred and fourteen grammes of powdered samarskite were kept for 3 weeks in a sealed glass tube. The air was pumped out and tested. It was found to contain about $\frac{1}{150}$ part of the emanation, which could have been extracted by heat.

A similar experiment with malacone showed that about one-fiftieth of its emanation was able to escape in the cold.

It appears, therefore, that these minerals retain nearly all their emanation. The same is probably true of the helium produced by the emanation. Samarskite which had been heated to redness was found to retain its emanation in the cold about as well as before.

PART II.

I happened to possess a small sample of a red deposit, coloured by iron, which is left by the water of the King's Spring, at Bath. It occurred to me that it might be worth while to test this for radio-activity. The result was to show that the deposit was markedly active. On leaving it in the testing vessel (which was closed airtight) for a few days, the activity was found to increase to several times its initial value. This shows that the deposit gives off an emanation freely, even without heat.

Experiments were then made to test the rate of decay of this

emanation. It proved to be identical with the rate of decay of the emanation of radium.* The activity is wholly due to that element.

This deposit was collected inside the King's Well itself, where the hot water issues from the ground. Other deposits are left in the tanks and pipes. They are less active than that collected near the source.

Deposits from another of the hot springs at Bath, that known as the Old Royal Spring, have also been tested. These were found to be active also. In this case there was no opportunity of collecting the deposit at the well-head itself, but it was found that the deposit left in the channel near the source was more active than that in the tanks further from it.

It was interesting to determine whether the water itself contained any radium in solution. There could be little doubt that there must be traces left in solution, after the deposit had settled out. But, since the Bath water contains abundance of sulphates, and since radium sulphate is one of the most insoluble salts known, there could not be more than the merest traces present. The sulphate of barium is very much less soluble than that of strontium. And presumably the sulphate of radium is much less soluble still. Barium sulphate requires half a million times its weight of water to dissolve it; radium sulphate perhaps several hundred million times its own weight.

About 10 litres of the Bath water were evaporated to dryness. The resulting saline residue was sealed up in a hard-glass tube, and left for about a fortnight to generate a stock of emanation. On heating, a distinct emanation was obtained, giving several times the rate of leak that air did. A deposit, similar to that from the Bath water, but black in colour, can be collected from the source of the hot springs of Buxton. It has been analysed by Dr. J. C. Thresh,† and I am indebted to his kindness for a specimen of it. This deposit was found to contain radium also; the proportion present being not very different from what was found in the case of some of the Bath deposits.

The following table gives the quantitative data for these emanations from these deposits. The rates of leak are on the same scale as those in the preceding table.

It will be seen that the richest of the deposits is some thirty-six times more active than the salt obtained by evaporating the water.

Although the agreement in the rate of decay of the emanation

* In the first experiment made, I obtained a small residual leak when the radium emanation had decayed. This was attributed to a new emanation, of greater durability. But I have failed to repeat the experiment, and am forced to conclude that the leak was due to a failure of the quartz insulation, owing to the presence of moisture. It is very difficult to understand how this can have happened, for the gas was passed through drying tubes. When the rate of leak was tested with air in the apparatus, it had always a perfectly definite and constant small value.

† 'Proc. Chem. Soc.,' January 17, 1882.

Material.	Quantity taken in grammes.	Rate of leak due to emanation (sc. div. per hour).	Rate of leak due to emanation from 100 grammes.	Time in days taken by the emanation to fall to half its initial value.
King's Spring, Bath—				
Deposit from inside of well.....	10	250	2,500	3·60
„ tank	12	78·2	650	..
Saline residue from water	18	12·4	69	..
Old Royal Spring, Bath—				
Deposit from channel near well .	10	63·5	635	..
„ bottom of tank ..	15	60	400	..
Hard deposit from sides of tank ..	25	43	173	3·58
Buxton deposit	26	356	1,370	3·81

seemed sufficient to prove that the activity was really due to radium, yet it was thought desirable to show that the chemical properties of the active constituent were in agreement with this conclusion. Two hundred grammes of the richest deposit were treated with dilute sulphuric acid. The activity was all in the insoluble residue, which was dirty white in colour, and amounted to about half of the entire quantity of deposit. The residue was boiled with strong sodium carbonate solution. This was washed away, and the mass extracted with hydrochloric acid. The hydrochloric acid solution gave a slight precipitate with sulphuric acid. This precipitate was collected, and found to be strongly active, so that there is every reason to conclude that the activity of the deposit is due to the presence of radium.

The presence of radium in the Bath water and deposits is of special interest because of the occurrence of helium in the gas which rises with the spring.* There can be little doubt that the helium owes its origin to the same store of radium that supplies the water.

It is interesting to estimate the quantity of radium annually delivered by the spring. Part of this is in the deposit. Part in the water. But the annual yield of deposit does not exceed a few hundred-weight at the most. And although it is much richer in radium than the dissolved salt, the quantity of the latter is so enormously greater, that the deposit may be neglected. According to the estimate of Sir A. C. Ramsay, the late Director of the Geological Survey, the salt annually delivered by the spring would be equivalent in volume to a column 9 feet in diameter, and 140 feet high. Taking the density to be twice that of water, this would weigh about 500,000 kilogrammes.

* Rayleigh, 'Roy. Soc. Proc.,' vol. 60, p. 56.

Now the saline residue gives about $\frac{1}{1500}$ part of the quantity of emanation that samarskite gives. Let us assume that the latter contains one-millionth part of radium, which is, I think, an outside estimate. At that rate, the annual delivery of radium by the spring amounts to about one-third gramme. The volume of gas which the spring delivered is about 100 cubic feet per day.* About $\frac{1}{1000}$ part of this is helium, so that about 3 litres of helium is given off daily, or about 1,000 litres per annum. The proportion of helium to radium thus indicated is of the same order as in the radio-active minerals, though somewhat larger. This is in accordance with the view that the spring draws its supplies from the disintegration of such minerals.

In obtaining the various materials from the Bath springs, I have had the great advantage of Mr. Sydenham's help. His knowledge of everything connected with the springs has been of great assistance.

In addition to the Bath and Buxton waters I have examined several others. A sample of the Cheltenham saline water, and also a deposit left in the pipes, was kindly sent me by Mr. G. Ballinger. But no emanation could be obtained, either from the dissolved salts or from the deposit. The boiler crust from a domestic hot-water pipe, Terling, Essex, was examined, but the result was again negative.

* Williamson 'B.A. Reports,' 1865, p. 380.